

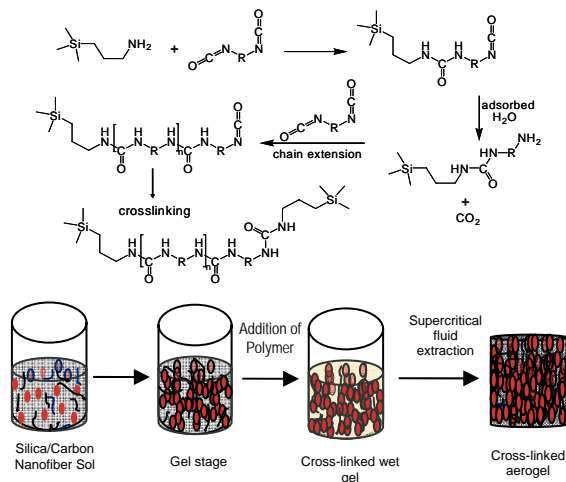
CARBON NANOFIBER INCORPORATED SILICA BASED AEROGELS WITH DI-ISOCYANATE CROSS-LINKING

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Introduction

Lightweight materials with excellent thermal insulating properties are highly sought after for a variety of aerospace and aeronautic applications.¹ Silica based aerogels with their high surface area and low relative densities are ideal for applications in extreme environments such as insulators for the Mars Rover battery.² However, the fragile nature of aerogel monoliths prevents their widespread use in more down to earth applications. We have shown that the fragile aerogel network can be cross-linked with a di-isocyanate via amine decorated surfaces to form a conformal coating.³ This coating reinforces the neck regions between secondary silica particles and significantly strengthens the aerogels with only a small effect on density or porosity. **Scheme 1** depicts the cross-linking reaction with the di-isocyanate and exhibits the stages that result in polymer cross-linked aerogel monoliths.



Scheme 1. Mechanism of incorporating fiber into amine modified silica aerogels and cross-linking with di-isocyanate

Composites of fiber and silica aerogels have been produced in a number of ways as an attempt to fortify the structure. Aerogel composites have been made by introducing a sol into a fibrous batting reinforcement,⁴ incorporating non-woven polypropylene fibers,⁵ or with non-woven carbon or silica fiber preforms for enzyme encapsulation.⁶ Silica aerogels have been reinforced with 5 to 25 w/w% ceramic fibers, reporting increased hardness, compressive strength, and elastic modulus of the monoliths as well as less shrinkage on supercritical drying.⁷ Finally, Lu et al have incorporated carbon nanofibers into uncross-linked silica aerogels to produce aerogel composites which were pyrolyzed for transformation into SiC/silica nanocomposites.⁸ However, no mechanical characterization of the composites was reported to demonstrate if carbon nanofibers were an effective reinforcement for the silica aerogels themselves.

In our current research, we examine the effect of integrating carbon nanofibers into the silica aerogel matrix for added structural integrity. The carbon fibers used are Pyrograf®-III nanofibers, a highly graphitic, low-cost carbon nanofiber. The base fibers were subjected to a proprietary oxidation process to give about 5 atom % singly bonded oxygen (combination of ether, epoxide, and alcohol) by XPS analysis. An SEM of the nanofibers is shown in **Figure 1**.

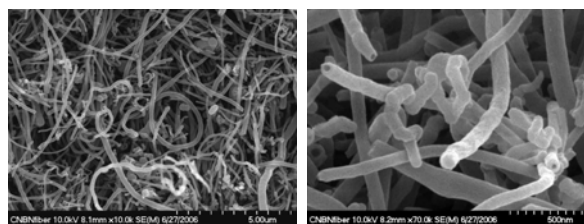


Figure 1. Scanning electron micrographs of Pyrograf III nanofibers.

A statistical experimental design approach was utilized to produce and analyze a series of cross-linked aerogels using different concentrations of silica precursors, di-isocyanate crosslinker and 0 to 5 w/w % carbon nanofibers in the silica backbone before cross-linking. In all, 19 separate formulations were prepared and characterized and the results analyzed by multiple linear regression.

Experimental

Materials. Tetramethorthosilicate (TMOS), 3-aminopropyltriethoxysilane (APTES) and anhydrous acetonitrile (CH_3CN) were purchased from Aldrich Chemical Company and used without further purification. Desmodur N3200 (1,6-hexamethylene diisocyanate-based oligomer) was provided by Bayer Corporation. Pyrograf®-III carbon nanofibers (PR-24-XT-LHT) were provided by Applied Sciences, Inc (ASI).

Procedure. Aerogels were prepared as previously described³ using a sol-gel process except that carbon nanofibers, in an amount equal to 0 to 5% of the theoretical weight of the silica in the gel was added to the silane solution and sonicated for approximately one half hour. To the stable suspension, water in acetonitrile was added to the silanes. The resulting solution was vigorously mixed and immediately poured into molds. Gelation occurred usually within 15 to 30 minutes. The gels were aged for 24 hrs before extracting into clean solvent. After exchanging with clean solvent three more times, the wet gels were soaked for 24 hrs in a di-isocyanate/acetonitrile solution followed by heating at 75°C to cross-link. After four additional solvent exchanges, the gels were dried by supercritical CO_2 fluid extraction.

Results and Discussion

SEM of a fracture surface of a typical low density aerogel monolith (no fiber) is shown in **Figure 2a**. In comparison, a micrograph of a monolith of similar density produced under similar conditions but containing 5 w/w % fiber is shown in **Figure 2b**. The structure of the aerogel is similar to the non-fiber containing sample, but the fibers clearly stand out as the diameters of the fibers are about an order of magnitude larger than the fine structure of the aerogel. In places, the aerogel appears to be intimately wrapped around the fibers, while in others the fiber is free of aerogel. For comparison, higher density aerogels are shown in **Figures 2c** (without fiber) and **2d** (with fiber).

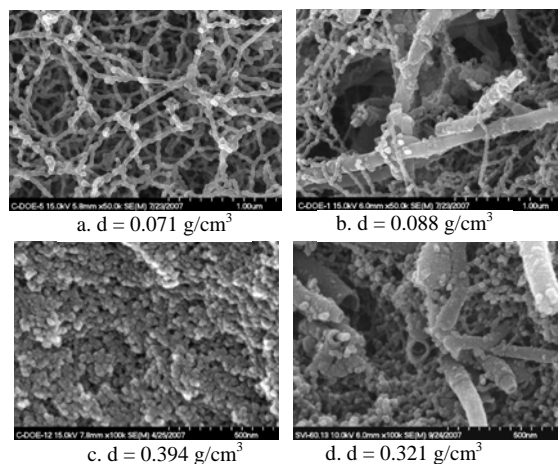


Figure 2. Scanning electron micrographs of monoliths with no fiber (left) and with fiber (right).

Figure 3 illustrates the response surface model for density vs. percent di-isocyanate and total silane. As is evident from the graph and in agreement with previous studies, the most influential variable on density of the aerogels is total silane concentration (total molar amount of APTES and TMOS). Also, density slightly decreases with increasing di-isocyanate concentration at low total silane, while at high total silane, increasing di-isocyanate increases density. Most notably, there was no significant effect of fiber concentration on density over and above random error.

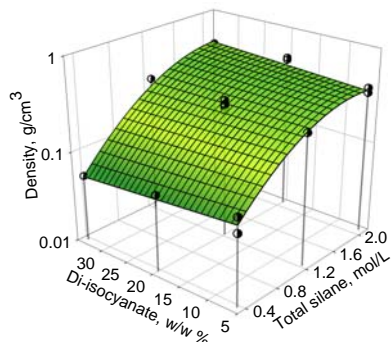


Figure 3. Empirically derived graphs showing density vs. total silane and fiber concentration.

Graphs of response surface models for Young's modulus which were extracted from compression tests are shown in **Figure 4** (top). Once again, the most dominant effect on the measured property is the total silane concentration followed by an effect of di-isocyanate concentration. Overall, maximum modulus values are achieved when density is at a maximum.

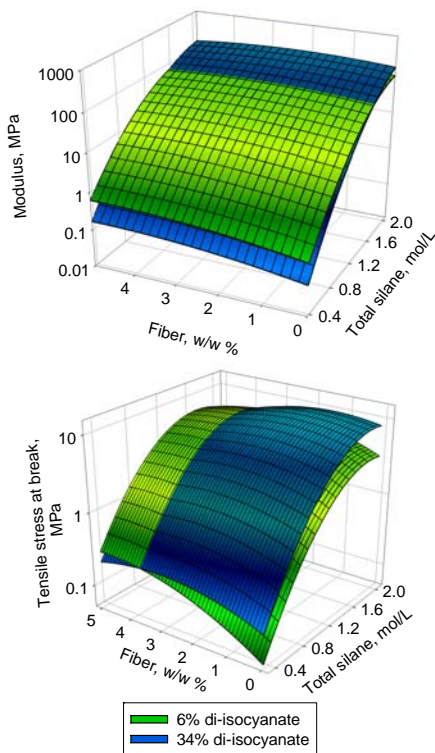


Figure 4. Empirically derived graphs showing modulus from compression vs. total silane concentration and fiber concentration (top) and tensile stress at break vs. total silane and fiber concentration (bottom).

However, the model indicates that increasing fiber concentration heightens modulus, especially at low total silane concentration. Hence, it is possible to obtain a three-fold increase in modulus from 0.2 MPa to 0.6 MPa by going

from 0 to 5% fiber at low total silane concentration while not increasing density.

The response surface model for tensile stress at break (**Figure 4**, bottom) is also dominated by total silane concentration although both fiber and di-isocyanate concentration are also significant terms in the model. When di-isocyanate concentration is high, tensile stress at break reaches a maximum at approximately 2 % fiber for all levels of total silane. The maximum value for tensile stress at break across the whole study is predicted to be 9.1 MPa when silane and di-isocyanate are both at the highest values studied and 1.8 w/w % fiber is used. It may be that when di-isocyanate concentration is high and especially when total silane is also high; the effect of the fiber is smaller because the large amount of polymer cross-linking toughens the aerogel structure enough to mask any further improvement due to the fibers. When di-isocyanate concentration is low, the effect of fiber is much more pronounced especially when total silane is also low. In fact, at low total silane and di-isocyanate concentration, stress at break is predicted to be five times higher when fiber concentration goes from 0% fiber (0.07 MPa) to 5% fiber (0.36 MPa). This improvement in tensile strength comes with no penalty in increased density or decreased porosity, as these responses are unaffected by the amount of carbon nanofiber present.

Conclusions

We have examined the effect of including up to 5 w/w % carbon nanofibers in the silica backbone of di-isocyanate cross-linked silica aerogels. Most notably, a three-fold increase in compressive modulus with 5% fiber was observed for aerogels made from the lowest total silane concentration with no increase in density. Similarly, a five-fold increase of tensile stress at break is predicted by including 5% fiber when total silane and di-isocyanate concentration are at a low. At higher levels of total silane and low di-isocyanate concentrations, there is still an increase in tensile stress at break but it is not as pronounced. When both total silane and di-isocyanate concentration are high, tensile stress at break reaches a maximum when 2 w/w % fiber is used. Since some agglomeration of fiber was observed in the dried aerogels at higher fiber loading, it may also be that better dispersion would result in greater improvement of mechanical properties.

No effect was seen on the density or porosity of the aerogels. Hence, the improvements in modulus and tensile strength due to fiber do not compromise other important properties of the aerogels. Perhaps the biggest impact of including carbon fiber in the aerogels may be an improvement in the strength of the initial hydrogels before cross-linking. Extracting the wet gels from the molds resulted in no breakage of the fiber containing gels, while nearly half of the gels from the lowest density runs with no fiber broke on initial extraction. This may have implications in large scale manufacturing of the lower density polymer cross-linked aerogels.

Acknowledgements We thank Demetrios Papadopolous of University of Akron for running compression tests and Dr. Brad Lerch for consultation in running tensile tests. Financial support from NASA's Subsonics Program and Advanced Extravehicular Activities Program (AEVA) is gratefully acknowledged. We also thank Bayer Corporation for providing the di-isocyanate oligomers and Applied Sciences, Inc. for the carbon nanofiber.

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CARBON NANOFIBER INCORPORATED SILICA BASED AEROGELS WITH DI-ISOCYANATE CROSS-LINKING

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Carbon Nanofiber Incorporated Silica Based Aerogels with Di-isocyanate Cross-linking

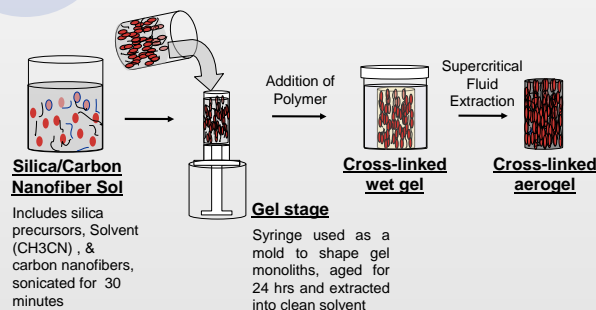


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Introduction

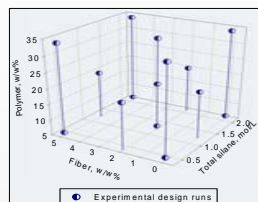
Silica based aerogels have been of significant interest to the aeronautics and aerospace industries due to their light weight and low thermal conductivity. Unfortunately, being primarily made of silica, the native aerogel tends to be extremely fragile. By incorporating an amine functionalized silica precursor, we are able to chemically modify the surfaces of secondary particles of the aerogel. These surface amines accommodate a conformal polymer coating to structurally enhance the weak neck regions which form the bead-like assembly associated with aerogels. To further enhance the structural integrity of the cross-linked aerogel, we have added carbon nanofibers to the silica matrix. The fibers have been oxidized using a proprietary process to provide surface ethers, epoxides and alcohols to promote good interface between matrix and nanofiber.



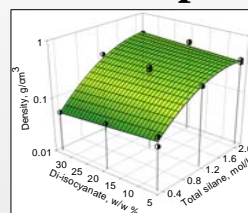
Pyrograf® III carbon nanofibers were incorporated into the sol consisting of acetonitrile, APTES and TMOS by sonication prior to hydrolysis.

Design of Experiments

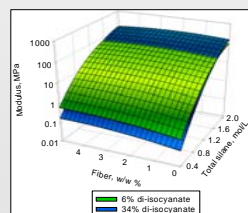
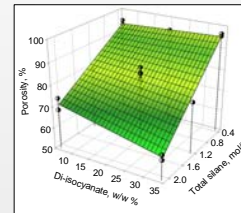
Statistical experimental design approach was utilized to reduce the number of experiments to assess the effects of different concentrations of the silica precursors, di-isocyanate, and carbon nanofibers on properties of resulting composite aerogels



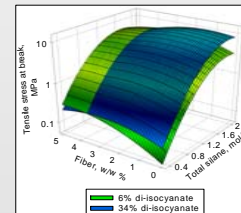
Empirical Models



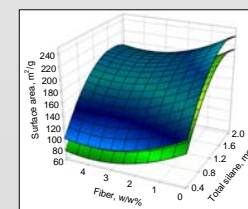
Fiber has no effect on density or porosity



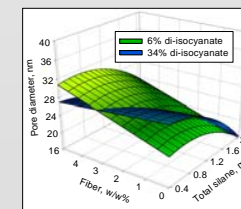
In low density samples, increasing fiber concentration from 0 to 5% increases modulus by factor of three



Tensile Stress at break increases with increasing fiber by as much as a factor of five.

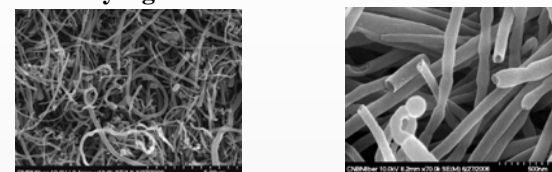


Surface areas show a small but significant decrease with increasing fiber concentration



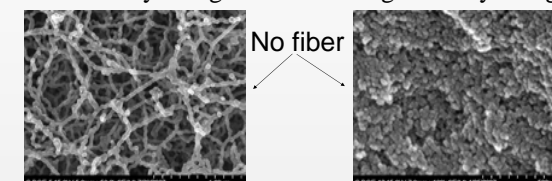
At low di-isocyanate concentrations, pore diameter has linear increase with increasing fiber

Pyrograf® III Carbon Nanofibers

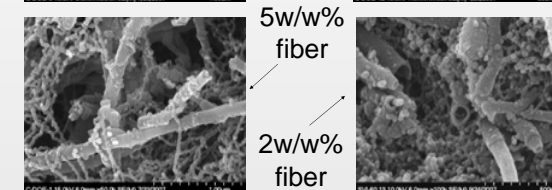


Low density aerogel

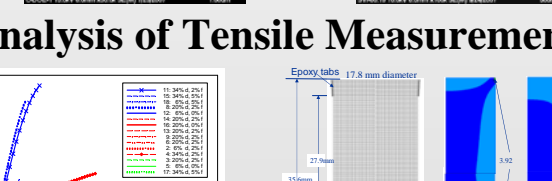
High density aerogel



No fiber

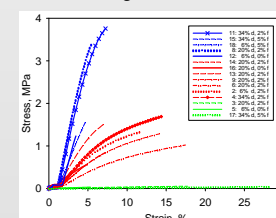


5w/w% fiber

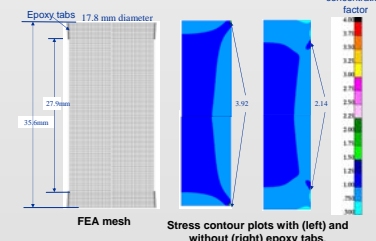


2w/w% fiber

Analysis of Tensile Measurements



Stress-strain plots from tensile tests with $s = 2.091 \text{ mol/L}$ (blue), $s = 1.23 \text{ mol/L}$ (red) and $s = 0.369 \text{ mol/L}$ (green)



Non-ideal cylindrical specimens used for tensile. Finite element analysis (FEA) used to calculate area of peak stress and stress concentration factor for each specimen. Adjusted stress at break calculated from measured value \times stress concentration factor.

Conclusions

- Three-fold increase in compressive modulus with 5% fiber - lowest density aerogels
- Five-fold increase in tensile stress at break shown by including 5% fiber at low density
- Some agglomeration of fiber was observed in aerogels at higher fiber loading, better dispersion may give greater improvement of mechanicals
- No effect of fiber was seen on density or porosity
- Improvements in modulus and tensile strength due to fiber do not compromise other important properties of the aerogels.
- Strength of initial hydrogels before cross-linking also improved by fiber—may have implications in large scale manufacturing of the lower density aerogels.

Acknowledgement: We thank Dan Scheiman (QSS) for running thermal analysis, and Baochun Nguyen (OAI) for helpful suggestions. We also thank Applied Sciences, Inc for supplying the Pyrograf fiber and Bayer Corporation for supplying Desmodur N3200. We gratefully acknowledge funding from the NASA Glenn Alliance for Technology Exchange (GATE), the Fundamental Aeronautics Program and the Exploration Systems Mission Directorate Student Internship Program.